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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE SULFAMIDE (T-BUNH)2S---ETC(U)

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$c = 12.076(6) \text{ \AA}$, $\beta = 90.46(4)^\circ$, and $Z = 4$. The symmetry of $(t\text{-BuNH})_2\text{SO}_2$ is C_2 , and the $t\text{-Bu}$ groups have a distal relationship with respect to each other.

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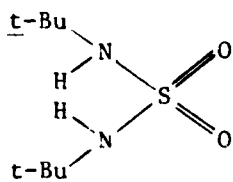
Contribution from the Departments of
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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE SULFAMIDE (t-BuNH)₂SO₂.

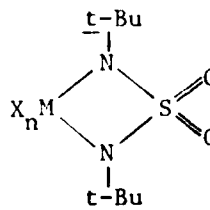
J. L. Atwood,*¹ A. H. Cowley,*² W. E. Hunter,¹ and S. K. Mehrotra²

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It has been demonstrated recently³ that the sulfamide, (t-BuNH)₂SO₂
(1), is a very useful precursor for the synthesis of novel heterocycles
such as 2.



1



2

e.g. M = P; X = Cl, n = 1

M = P; X = F, n = 1

M = P; X = NMe₂, n = 1

Interestingly, if the steric bulk of the N-alkyl group is reduced, it is not possible to isolate heterocycles like **2** and only polymeric materials or ring-opened products can be isolated.⁴ Apart from its relevance to the foregoing synthetic considerations, the structure of $(t\text{-BuNH})_2\text{SO}_2$ is also pertinent to discussions of the bonding in sulfur compounds.⁵ We are aware of only two previous X-ray crystal structures on sulfamides. The structure of the parent compounds, $(\text{H}_2\text{N})_2\text{SO}_2$, has been determined by Trueblood and Mayer,⁶ and that of the permethylated analogue, $(\text{Me}_2\text{N})_2\text{SO}_2$, has been reported by Lipscomb et al.⁷ The present work therefore represents the first single-crystal X-ray diffraction study of a symmetrical dialkylsulfamide.

EXPERIMENTAL SECTION

N,N'-ditertiarybutylsulfamide, $(t\text{-BuNH})_2\text{SO}_2$ (**1**), was prepared according to the method of Bermann and Van Wazer.⁸ Clear, colorless crystals of suitable for X-ray diffraction were grown by re-crystallization from a 6:1 $\text{CH}_2\text{Cl}_2/\underline{n}$ -pentane solution.

X-RAY CRYSTALLOGRAPHY. The data crystal was sealed under a dry nitrogen atmosphere in a 0.5 mm O.D. Lindemann glass capillary. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated MoK_α radiation. The diffracted intensities were collected by the ω - 2θ scan technique in a manner similar to that described previously.⁹ One independent quadrant of data was measured out to $2\theta < 44^\circ$, and a slow scan was performed on a total of 1242 unique reflections. The

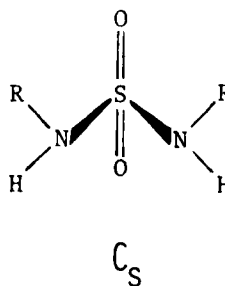
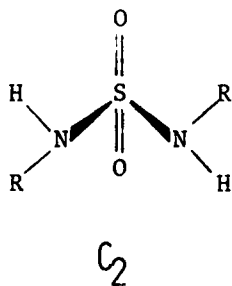
intensities were corrected for Lorentz and polarization effects but not for absorption. A summary of pertinent crystallographic parameters is presented in Table I.

The structure was solved using the direct methods program¹⁰ and refined using the SHELX system.¹¹ All hydrogen atoms were located on difference Fourier maps and allowed to ride on the bonded atom.

RESULTS AND DISCUSSION

The molecular structure and labeling scheme for $(t\text{-BuNH})_2\text{SO}_2$ (**1**) are shown in Figure 1 and a stereoview of the unit cell is provided in Figure 2. Bond distances and angles are presented in Table II, and the atomic positional and thermal parameters are listed in Tables III and IV, respectively.

Previous structural work on sulfamides^{6,7} has established the approximate orthogonality of the N-S-N and R-N-R planes.¹² An N,N'-dialkylsulfamide is therefore capable of existing in C_2 and C_s conformations.



The preference of $(t\text{-BuNH})_2\text{SO}_2$ for the C_2 conformation (Figure 1) presumably stems from minimization of the steric interactions between the

t-Bu groups. The steric demands of the t-Bu groups are also evident in the following structural features: (i) the N-S-C bond angles in **1** ($127.4(2)^\circ$) are significantly larger than those in $(\text{Me}_2\text{N})_2\text{SO}_2$ ($117.9(4)$ and $119.7(4)$),⁷ and (ii) the normals to the C-N-H and N-S-N planes in **1** are 101.8° , while those to the C-N-C and N-S-N planes in $(\text{Me}_2\text{N})_2\text{SO}_2$ are 89.4° .

Unfortunately, structural data are not available for other N,N'-disubstituted sulfamides. However, it seems reasonable to conjecture that the energy difference between the ζ_2 and ζ_s conformations will decrease as the steric bulk of the alkyl moiety diminishes. In turn, the less rigid nature of a sulfamide such as $(\text{MeNH})_2\text{SO}_2$ may be a factor in the tendency of this molecule to form polymers rather than discrete heterocycles when treated with active halides.

The sums of the bond angles at nitrogen in **1** are 357.3 and 353.2° at N(1) and N(2), respectively. The geometry at nitrogen is thus between trigonal planar and tetrahedral, but nearer to trigonal planar. A similar nitrogen geometry was found in $(\text{Me}_2\text{N})_2\text{SO}_2$ ($\Sigma_N = 350.5^\circ$). The S-N bond distances in **1** are $1.615(2)$ and $1.616(2)$ Å and thus substantially less than the sum of the covalent radii for sulfur and nitrogen (1.75 Å).¹³ Similar S-N bond shortening has been observed in the sulfamides $(\text{NH}_2)_2\text{SO}_2$ ($1.600(9)$ Å) and $(\text{Me}_2\text{N})_2\text{SO}_2$ ($1.623(5)$ Å). Trigonal planar or near trigonal planar nitrogen geometries and short N-element bond distances are an increasingly familiar feature of the structures of many N-S and N-P compounds.¹⁴ Such observations are not inconsistent with the postulate of d-orbital participation on the part of sulfur or phosphorus. However,

it is not possible to be unequivocal on this point since, for example, some of the N-element "bond shortening" is due to the predication of the nitrogen covalent radius on the assumption of tetrahedral rather than trigonal planar geometry.

The geometry of the O_2SN_2 unit varies very little in **1**, $(H_2N)_2SO_2$, and $(Me_2N)_2SO_2$. Like the S-N bond distances, the S-O bond distances of these sulfamides fall in the order $(Me_2N)_2SO_2$ (1.441(5) and 1.449(5) Å) > **1** (1.434(2) Å) > $(H_2N)_2SO_2$ (1.391(8) Å). This ordering follows the electronegativities of the amide groups.

ACKNOWLEDGEMENT. The authors are grateful to the Office of Naval Research (Contract N00014-76-C-0577, Task No. NR 053-612) and the National Science Foundation (Grants CHE79-10155 and CHE78-09729) for generous financial support.

SUPPLEMENTARY MATERIAL AVAILABLE. A table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

REFERENCES AND NOTES

- (1) University of Alabama.
- (2) University of Texas at Austin.
- (3) Cowley, A. H.; Mehrotra, S. K.; Roesky, H. W. Inorg. Chem. **1981**, 20, 712-716.
- (4) Roesky, H. W.; Mehrotra, S. K.; Platte, C.; Amirzadeh-Asl, D.; Roth, B. Z. Naturforsch., B: Anorg. Chem. Org. Chem. **1980**, 35B, 1130-1136.
- (5) See, for example, Kwart, H.; King, K. G. "d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur", Springer-Verlag, New York, 1977.
Cruickshank, D. W. J. J. Chem. Soc. **1961**, 5486-5504; Cilento, G. Chem. Rev. **1960**, 60, 147-167.
- (6) Trueblood, K. N.; Mayer, S. W. Acta Crystallogr. **1956**, 9, 628-634.
- (7) Jordan, T.; Smith, H. W.; Lohr, L. L., Jr.; Lipscomb, W. N. J. Am. Chem. Soc. **1963**, 85, 846-851.
- (8) Bermann, M.; Van Wazer, J. R. Synthesis **1972**, 576-577.
- (9) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. J. Chem. Soc. Dalton Trans. **1979**, 45-53.
- (10) Germain, G.; Main, P.; Woolfson, M. M. Acta Crystallogr., Sect. A **1971**, A27, 368-376.
- (11) Sheldrick, G. SHELX 76, program system for crystal structure determination, 1976.
- (12) This observation has been ascribed by Lipscomb et al.⁷ to the optimization of both $N \rightarrow S$ and $O \rightarrow S$ $p\pi-d\pi$ bonding in this conformation. Rotation of the NR_2 groups by 90° would result in increased competition of the N and O lone pairs for the available S(3d) orbitals.

- (13) Pauling, L. "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, NY, 1960.
- (14) For example, $d_{\text{SN}} = 1.648(2) \text{ \AA}$ in $(\text{Me}_2\text{N})_2\text{SF}_2$ (Cowley, A. H.; Riley, P. E.; Szobota, J. S.; Walker, M. L. J. Am. Chem. Soc. **1979**, 101, 5620-5624). For a discussion of this phenomenon in aminophosphines, see Cowley, A. H.; Davis, R. E.; Remadna, K. E. Inorg. Chem. **1981**, 20, 0000, and references therein.

TABLE I. Pertinent Crystallographic Parameters for (t-BuNH)₂SO₂

cryst system	monoclinic
space group	P2 ₁ /c
cell const	9.720(3)
a, Å	9.720(3)
b, Å	9.887(3)
c, Å	12.076(4)
β, deg	90.46(3)
cell vol, Å ³	1160.5
Z	4
density (calcd), gcm ⁻³	1.19
observed reflections	1242
R	0.030
R _w	0.036
μ, cm ⁻¹	2.53

TABLE II. Bond Distances (Å) and Bond Angles (deg) in (t-BuNH)₂SO₂

S	-	O(1)	1.434(2)	S	-	O(2)	1.434(2)
S	-	N(1)	1.615(2)	S	-	N(2)	1.616(2)
N(1)	-	C(1)	1.492(4)	N(2)	-	C(5)	1.496(4)
N(1)	-	H(1)	1.00	N(2)	-	H(11)	1.03
C(1)	-	C(2)	1.517(4)	C(1)	-	C(3)	1.518(4)
C(1)	-	C(4)	1.522(5)	C(5)	-	C(6)	1.533(4)
C(5)	-	C(7)	1.519(4)	C(5)	-	C(8)	1.528(4)

O(1)	-	S	-	O(2)	118.7(1)	O(1)	-	S	-	N(1)	110.6(1)
O(2)	-	S	-	N(1)	104.5(1)	O(1)	-	S	-	N(2)	103.6(1)
O(2)	-	S	-	N(2)	108.6(1)	N(1)	-	S	-	N(2)	110.8(1)
S	-	N(1)	-	C(1)	127.4(2)	S	-	N(2)	-	C(5)	127.5(2)
C(1)	-	N(1)	-	H(1)	116.6	C(5)	-	N(2)	-	H(11)	112.3
H(1)	-	N(1)	-	S(1)	113.3	H(11)	-	N(2)	-	S(1)	113.4
N(1)	-	C(1)	-	C(2)	111.4(2)	N(1)	-	C(1)	-	C(3)	105.2(2)
C(2)	-	C(1)	-	C(3)	109.5(3)	N(1)	-	C(1)	-	C(4)	110.5(3)
C(2)	-	C(1)	-	C(4)	110.2(3)	C(3)	-	C(1)	-	C(4)	109.9(3)
N(2)	-	C(5)	-	C(6)	103.9(2)	N(2)	-	C(5)	-	C(7)	111.4(2)
C(6)	-	C(5)	-	C(7)	109.9(3)	N(2)	-	C(5)	-	C(8)	111.0(2)
C(6)	-	C(5)	-	C(8)	110.0(3)	C(7)	-	C(5)	-	C(8)	110.4(3)

TABLE III. Atomic Positions in Fractional Coordinates for $(t\text{-BuNH})_2\text{SO}_2$

Atom	x/a	y/b	z/c
S	0.24896(7)	0.51174(7)	0.51535(5)
O(1)	0.3536(2)	0.6072(2)	0.5462(2)
O(2)	0.1408(2)	0.4840(2)	0.5922(1)
N(1)	0.1702(2)	0.5601(2)	0.4039(2)
C(1)	0.2237(3)	0.6516(3)	0.3159(2)
C(2)	0.3679(3)	0.6117(4)	0.2817(3)
C(3)	0.1257(4)	0.6340(4)	0.2184(3)
C(4)	0.2218(4)	0.7979(4)	0.3530(3)
N(2)	0.3336(2)	0.3738(2)	0.4940(2)
C(5)	0.2792(3)	0.2428(3)	0.4498(2)
C(6)	0.3846(3)	0.1378(3)	0.4898(3)
C(7)	0.1386(3)	0.2105(3)	0.4971(3)
C(8)	0.2729(4)	0.2443(4)	0.3234(2)
H(1)	0.0685(2)	0.5492(2)	0.4074(2)
H(2)	0.3935(3)	0.6717(4)	0.2197(3)
H(3)	0.4378(3)	0.6208(4)	0.3385(3)
H(4)	0.3693(3)	0.5175(4)	0.2586(3)
H(5)	0.1492(4)	0.6936(4)	0.1605(3)
H(6)	0.1232(4)	0.5354(4)	0.1923(3)
H(7)	0.0312(4)	0.6513(4)	0.2425(3)
H(8)	0.2597(4)	0.8626(4)	0.2907(3)
H(9)	0.2814(4)	0.8074(4)	0.4224(3)
H(10)	0.1253(4)	0.8242(4)	0.3733(3)
H(11)	0.4350(2)	0.3900(2)	0.4724(2)
H(12)	0.3775(3)	0.1291(3)	0.5747(3)
H(13)	0.4812(3)	0.1587(3)	0.4620(3)
H(14)	0.3598(3)	0.0548(3)	0.4614(3)
H(15)	0.0596(3)	0.2761(3)	0.4693(3)
H(16)	0.1445(3)	0.2114(3)	0.5830(3)
H(17)	0.1166(3)	0.1198(3)	0.4757(3)
H(18)	0.2491(4)	0.1557(4)	0.2944(2)
H(19)	0.3635(4)	0.2656(4)	0.2971(2)
H(20)	0.2017(4)	0.3112(4)	0.2990(2)

TABLE IV. Thermal Parameters^a for (t-BuNH)₂SO₂

Atom	B11	B22	B33	B12	B13	B23
S	0.00576(8)	0.00794(9)	0.00460(5)	0.00004(7)	0.00008(5)	-0.00032(5)
O(1)	0.0073(2)	0.0090(3)	0.0069(2)	-0.0010(2)	-0.0006(2)	-0.0015(2)
O(2)	0.0073(2)	0.0110(3)	0.0052(1)	0.0004(2)	0.0014(1)	0.0001(2)
N(1)	0.0053(3)	0.0098(3)	0.0057(2)	0.0000(2)	-0.0001(2)	0.0017(2)
C(1)	0.0087(4)	0.0106(4)	0.0058(2)	-0.0006(3)	0.0002(2)	0.0020(3)
C(2)	0.0097(4)	0.0130(6)	0.0077(3)	-0.0009(4)	0.0021(3)	0.0030(3)
C(3)	0.0133(5)	0.0194(6)	0.0073(3)	-0.0024(5)	-0.0025(3)	0.0047(3)
C(4)	0.0102(6)	0.0106(5)	0.0109(4)	-0.0008(4)	0.0009(4)	0.0024(3)
N(2)	0.0056(3)	0.0079(3)	0.0060(2)	0.0005(2)	-0.0005(2)	-0.0002(2)
C(5)	0.0085(4)	0.0075(3)	0.0063(2)	0.0000(3)	-0.0008(2)	-0.0006(2)
C(6)	0.0122(5)	0.0080(4)	0.0112(3)	0.0017(3)	-0.0020(3)	-0.0002(3)
C(7)	0.0095(4)	0.0103(4)	0.0098(3)	-0.0027(3)	-0.0000(3)	-0.0012(3)
C(8)	0.0139(5)	0.0120(5)	0.0067(3)	0.0005(4)	-0.0008(3)	-0.0020(3)

^aAnisotropic thermal parameters defined by

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

FIGURE CAPTIONS

FIGURE 1. View of the $(\underline{t}\text{-BuNH})_2\text{SO}_2$ molecular structure showing the atom numbering scheme.

FIGURE 2. Stereoview of the unit cell for $(\underline{t}\text{-BuNH})_2\text{SO}_2$.

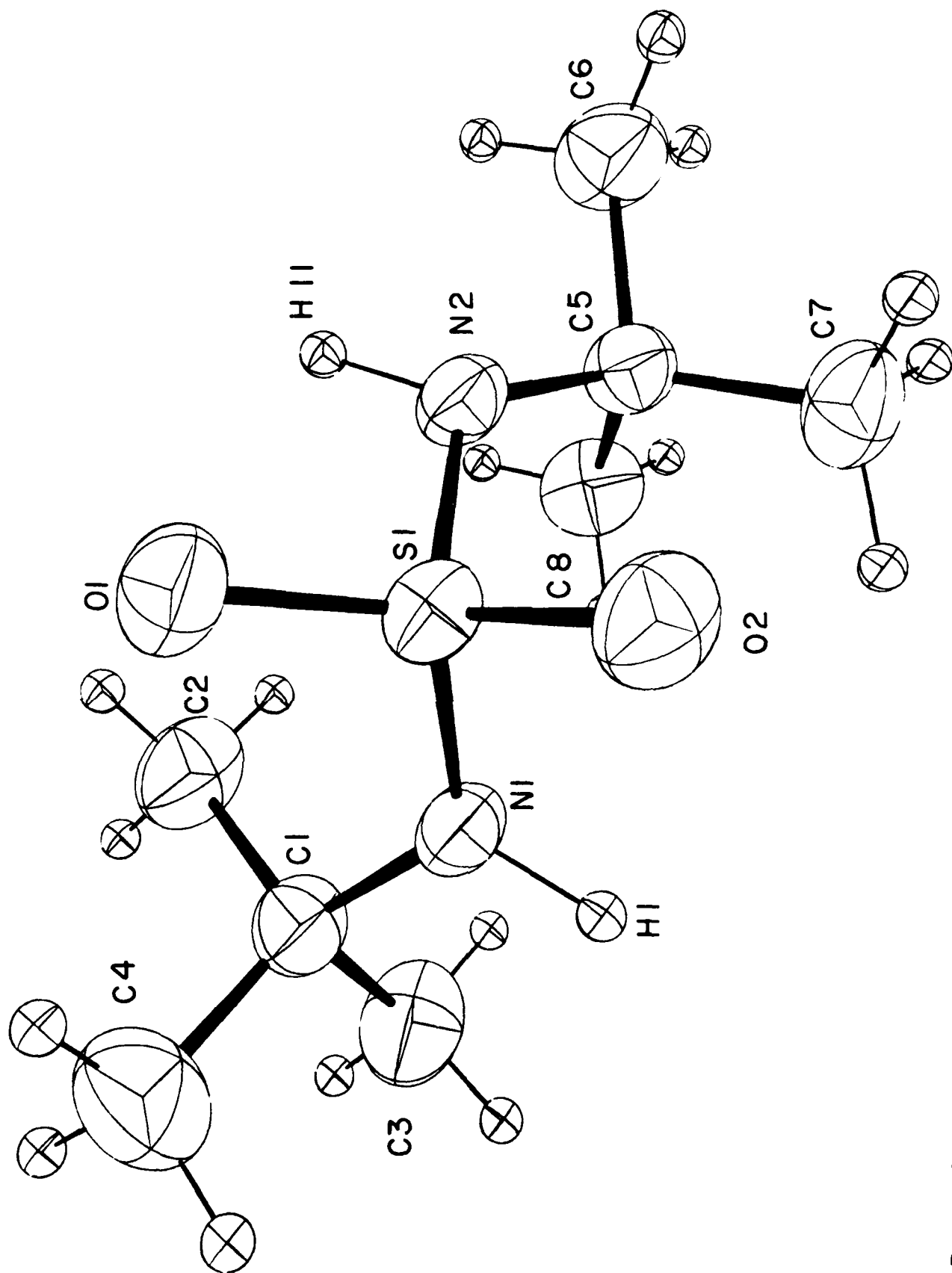


FIGURE 1

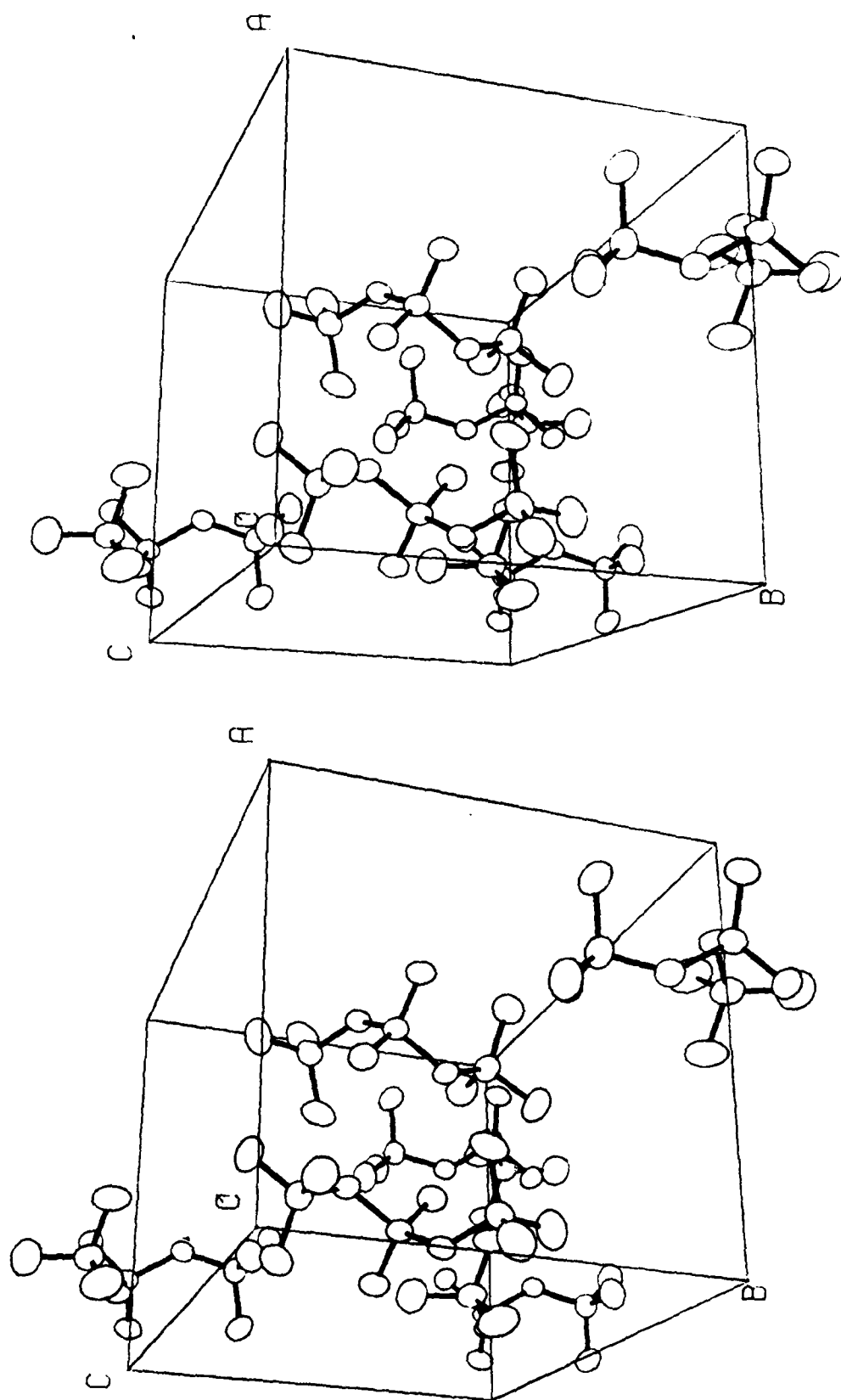


FIGURE 2